

METHOD FOR SELECTIVELY SEPARATING USED FRAGMENTATED
ORGANIC MATERIALS BY MEANS OF DENSE AQUEOUS SUSPENSIONS

Domain of the invention

The invention relates to a method for selectively separating mixed synthetic organic materials such as filled or unfilled polymers and / or copolymers in the form of wastes and particularly recyclable domestic wastes for reuse, these synthetic organic materials originating from the destruction of cars and obsolete durable consumer products at the end of their lives by grinding, the said selective separation method consisting of separating these materials at a chosen density threshold in a dense medium formed from non-viscous separative liquid suspensions which consist of powder particles dispersed in an aqueous phase and stabilised at a density threshold value chosen so as to provoke the selective separation of a determined fraction of the mixture of waste materials to be separated.

The waste synthetic organic materials concerned generally originate from the destruction of cars and obsolete durable consumer products at the end of their lives by grinding, in which a large number of different types of synthetic organic materials are present, including filled or unfilled polymers and / or copolymers, with or without fire retardant, with or without additives, are considered to be reusable, and in which a large number of other materials are considered as being unwanted contaminants such as metals, minerals and other various contaminants that must firstly be eliminated. Other wastes, such as mixed industrial wastes containing synthetic organic materials and packaging wastes such as polymers and / or copolymers originating from municipal tips and also containing mixed polymer materials can also be considered as being potentially reusable.

In industries for recycling waste synthetic organic materials to be reused, various methods are used for separating more or less polluting and more or less polluted stream constituents with a variable concentration of reusable synthetic organic materials that have to be separated from the pollutants, concentrated and sorted by homogeneous streams of the different types of synthetic organic materials present, for example such as polyethylene, polypropylene, polystyrene (PS), acrylonitrile-butadiene-styrene (ABS) copolymer, polyamides (PA), polyvinyl

chloride (PVC), polyesters, polyurethane, polycarbonate, acrylic or metacrylic or other copolymers, all polymers that may or may not be filled, used with additives, and with or without fire retardants.

These known methods can currently be used to extract and separate streams to be treated, composed of mixes of synthetic organic materials to be reused and contaminating materials to be eliminated, these streams including:

- ✓ a phase of synthetic organic materials with a density less than 1,
- ✓ a phase of synthetic organic materials with a density greater than or equal to 1,
- ✓ a phase of synthetic organic materials, for example consisting of polyethylene, polyurethane foams, film waste, wire waste and others,
- ✓ a phase of contaminating materials to be eliminated, consisting of constituents that cannot be reused in such separation and reuse methods, for example sand, glass debris, wood debris, remaining metals and others.

One of these methods for separation of all types of polymer materials originating from the destruction of cars and / or other objects at the end of their lives by grinding (described in European patent EP 0918606 B) consists of performing a grinding step to fragment synthetic organic materials, then preferably carrying out a mechanical separation based on a shape factor, followed by a first density separation step in which all synthetic organic materials to be reused are separated into two streams:

- ✓ the first with a density less than 1, particularly and for example including unfilled polyolefins such as polyethylenes ($d = 0.92$ to 0.95), polypropylenes (d about 0.9), ethylene and vinylacetate copolymers, ethylene-propylene rubber (E.P.R) copolymers, ethylene-propylene-diene-monomer (E.P.D.M.) copolymers, polyethylene (PE) foams, polypropylene (PP) foams, polyurethane (PU) foams and others,
- ✓ the other with a density greater than or equal to 1, and for example including particularly:
 - polystyrene: unfilled PS (d about 1.05)

- acrylonitrile-butadiene-styrene copolymers: unfilled ABS (d about 1.07)
- polyvinyl chlorides: unfilled rigid PVC (d about 1.30 to 1.40) and filled rigid PVC (d about 1.40 to 1.55), plastified PVC such as plastisol and PVC foams
- polycarbonates: unfilled PC with density $d = 1.20$ to 1.24 , filled PC reinforced with 20% glass fibre with density $d = 1.3$, or filled PC reinforced with 30% of glass fibres with density $d = 1.44$
- thermoplastic rubbers, except for thermosetting honeycombed rubbers
- polyurethanes: filled PU ($d =$ about 1.21)
- Talc-filled polypropylenes (PP/talc filled with between 5% and 40% of talc)
- filled polyethylenes: (Filled PE containing between 2% and 40% of fillers)
- unsaturated polyesters (d varying from about 1.10 to 1.13)
- saturated filled or unfilled polyesters ($d \geq 1.20$) (frequently filled with glass fibres)
- polyamides: filled or unfilled PA_6 ($d = 1.13$), $PA_{6,6}$ ($d = 1.14$), $PA_{6,10}$ ($d = 1.08$), PA_{11} ($d = 1.04$), PA_{12} ($d = 1.02$),
- polymethyl methacrylates: PMMA ($d = 1.18$)
- others.

These two streams are treated later to extract each component from them, to separate them into homogenous streams and treat them to make them into formulated pellets that can be used directly for plastic transformation processes.

If the stream of the mix of reusable synthetic organic materials with a density of less than 1 can be efficiently treated by a series of separation steps in aqueous medium using baths with an appropriate density to enable a fine selection of the different polymer compounds present in the said stream, this is not the case for the stream of the mixture of organic materials with a density greater than or equal to 1 for which it is difficult to separate the different synthetic organic materials.

For this second stream that is composed of a mix of filled or unfilled polymers and / or copolymers, with densities varying from 1 to about 1.6, the various

synthetic organic materials present in the mix are density separated in hydraulic separators in which the liquid separation medium consists of water, surfactants and mineral compounds such as clays and particularly bentonite and possibly compounds soluble in water such as mineral salts, compounds used to increase the density of the liquid phase and increase it until its density enables separation in principle of the various organic synthetic materials into two distinct phases, one supernatant and the other sinking in the bottom of the separator, each phase forming a new stream for which a new density separation is carried out in turn.

However it is found that the liquid separation media are not sufficiently stable in practice to enable accurate selective separations by density, in other words providing very homogeneous separations into types of sorted materials, particularly in density separation installations in use in industries for processing waste synthetic organic materials to be reused, since streams output from the separation can be mixes of several materials for which the corresponding densities are very similar to each other.

Several particularly annoying phenomena are observed that occur in these liquid density separation media; these annoying phenomena are genuine disadvantages, and are as follows:

- ✓ a variation of the rheology of the said liquid media, that is demonstrated by a disturbing variation of their viscosity towards a more fluid or a more pasty state,
- ✓ a drift or a variation of the apparent density of liquid media, since the density cannot remain stable at the initially chosen threshold for good separation of waste synthetic organic materials to be reused, this drift (variation) changing the composition of the streams separated by a dense liquid medium,
- ✓ settlement in time of a fraction of the mineral compounds dispersed in the aqueous medium to create the chosen density, partly causing the change in the density of the liquid separation medium,
- ✓ quasi-impossibility of accurately separating filled or unfilled waste synthetic organic materials to be reused, as soon as the density separation

of the different materials has to be done for a density difference $\Delta = |0.01|$, in other words within an interval around the chosen density "ds" equal to $ds \pm 0.005$.

Thus, there is an undoubted and important problem about very precise density separation of synthetic organic waste materials to be reused such as filled or unfilled polymers and / or copolymers, consisting of used wastes to be recycled originating from the destruction of cars and obsolete durable consumer products at the end of their lives by grinding, to obtain separated homogeneous material streams without a drift in the density and mix of the selected materials.

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State of the art

A large amount of research work has been done on the use a dense liquid medium to achieve the best possible separation of solid materials with a density equal to at least 1 or very much more than 1 and that are difficult from each other, and there are many industrial applications.

The dense liquid medium used in the state of the art with a density usually greater than 1 is formed of an aqueous phase in which:

- ✓ soluble mineral salts can be dissolved to increase the real density of the aqueous phase to achieve a required density,
- ✓ powder clays can be dispersed to create a suspension with an apparent density equal to the required density,
- ✓ both of the above mentioned means, namely solubilisation of salts to increase the density of the aqueous phase and the dispersion of clays in the higher density aqueous phase, can be combined to increase the stability of the suspension of clays in the densified aqueous phase, within the limit of what is possible.

For example, for the treatment of minerals, density methods carried out consist of performing a mechanical grinding action to the liberation mesh size and then separating the ore from the gangue in an aqueous suspension of dispersed powder clay, the clay acting as a densifying agent, in the appropriate concentration to

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enable separation of components to be separated into two phases, one supernatant phase and the other sinking.

However, the stability of the said suspensions at clay concentrations used to prepare densified separative suspensions is not very good because clay
5 concentrations can vary with time depending on the variation of the composition of the gangue present and to be eliminated for which the density is not constant and varies depending on the extraction zone, and the density of the ore to be extracted is not constant either and also varies depending on the extraction area.

The density threshold chosen for the separation is relatively coarse with these
10 methods, and usually the separation sensitivity cannot be better than a single decimal figure, in other words a densified separation medium for which the apparent density will be between 1.4 and 1.5.

For example, separation methods based on the use of dense liquid media are used, in which a sufficient quantity of mineral salts is dissolved in the aqueous phase
15 or a sufficient quantity of powder clays is dispersed in order to determine the separation threshold density in the presence of surfactants, for synthetic organic waste materials to be reused such as fragmentated polymer materials to be separated from each other or to be separated from their pollutants.

Documents have described such dense liquid separation media. A first
20 document (DE19964175) describes a technology for the separation of a heterogeneous mix of fragmentated polymer materials depending on their apparent density, in a saline aqueous solution forming the dense liquid medium with a predetermined density, the separation being done at laminar stream requiring optimisation of the stream conditions of the saline aqueous solution and the mix of
25 polymer materials to be separated.

The method thus described only appears suitable for a single density value because it appears difficult to vary the density of the dense liquid medium within a wide range of values, this variation being related to the fact that increasing concentrations of dissolved salts are necessary to achieve relatively high densities;
30 consequently, the operating cost of this method can then become unacceptable for the separation of waste synthetic organic materials with very low added value for reuse,

particularly because the technology used is affected by obvious corrosive action due to the saline liquid medium.

Another document (US 3 857 489) describes a method for separation of a stream of materials to be separated in a dense aqueous medium made using a powder clay suspension dispersed in water for which the stability is improved due to the addition of a water soluble hetero polysaccharide type of surfactant into the suspension to stabilise the clay. But the separative suspension is not sufficiently stable since a clay particles settlement phenomenon occurs which causes a large variation in the density threshold chosen for the selective separation.

As mentioned above, another document (EP 0918 606 B1) describes a method for the separation of fragmentated polymer materials originating from the destruction of cars and / or other objects at the end of their lives by grinding that uses separation on a stream composed of a mix of filled or unfilled polymers and / or copolymers with densities ranging from 1 to 1.6, in a dense liquid medium using a suspension made of a powder clay dispersed in water so as to obtain a density separation medium with a given density threshold. But as has been mentioned, such a separative suspension has disadvantages that are difficult to overcome, for example variation of the rheology and density with time, settlement of the powder clay and the impossibility of fixing a precise density threshold, for example as far as the second decimal figure, and maintaining it.

Another document (US 4 460 788 B1) describes a method of separating all categories of polymers originating from wastes including a grinding step, a mechanical separation step and two density separation phases in which the density varies upwards or downwards.

In the density separation phase, the liquid medium in the hydraulic separator contains an aqueous phase, a powder inorganic compound that is clay put in suspension to increase the density of water, and a wetting agent (based on a fatty alcohol modified with ethylene oxide and / or propylene oxide) that also maintains the inorganic compound in suspension. With this separation method, the size of particles in suspension is never mentioned either through a size grading cut-off or through a median diametric dimension of these particles; this lack of precision is a problem that particularly affects the stability of the suspension and more particularly

the stability of the density required for this suspension, due to the obvious segregation of the largest particles that sink to the bottom of the container.

Another document (US 6 335 376 B1) describes a method of separating polymers present in a mix of different polymers containing neither metals nor pollutants to be eliminated such as glass, foam, wood or other. The claimed method consists of heating the mix of these different polymers after dimensional selection, to cause bubbling of at least of the polymers of the said mix to be separated and then separating it from the said mix due to a change in the apparent density of the said polymer caused by heating.

This modification of the apparent density creates a differentiation between at least one of the polymers in the heated mix and the other polymers in the mix and a selective separation of alterations of the densities of each polymer in successive steps.

This method uses particular separation means that apply heat to destructure the polymer materials to be separated, instead of using an aqueous suspension of solid powder particles to create a separation density level.

Thus, the state of the art proposes different methods for the separation of materials, such as materials originating from the destruction of cars and / or durable consumer products at the end of their lives by grinding such as household appliances, electronic or other equipment which, after metals have been recovered, are synthetic organic materials, using dense liquid media with all the disadvantages mentioned above.

But the state of the art does not include any methods for the particularly precise separation of the different types of constituents with a density equal to at least 1 and usually much greater than 1, forming a mix of fragmentated synthetic organic waste materials to be reused.

Objectives of the invention

The industrial problem that arises after examining the state of the art and that appears even more insoluble after considering this state of the art, is to create a corresponding method and installation for precise separation by difference in density. Such a precise separation method can be achieved using a dense liquid medium of

complex mixes of all types of organic synthetic waste materials, to be separated into individual types, each with a density equal to at least 1, in order to reuse them by recycling, all these materials being filled or unfilled, thermoplastic or thermosetting polymers and / or copolymers.

5 Examples include all thermoplastics such as polyolefins and olefinic copolymers, PVC and derivatives, polystyrene and its copolymers, cellulose derivatives, polyamides, acrylic and other polymers, etc., and also thermosetting plastics such as unsaturated polyesters, cross linked polyurethanes, phenoplasts, aminoplasts, epoxy resins and others, etc., and all special polymers such as
10 polycarbonate, polyimides, linear polyurethanes, saturated polyesters, silicones, polymers containing fluoride or other polymers, synthetic and other elastomers, etc., these organic products possibly being used alone or mixed, but also possibly being modified by mineral fillers, reinforcing fibres, flame retarders, impact modifiers, colouring agents, heat and light stabilizers, lubricants, antistatic products, expansion
15 agents and others.

Many objectives are assigned to the invention, so that at least most of the disadvantages that appeared in the state of the art can be eliminated.

A first purpose of the invention is to create a method and its corresponding industrial installation for selectively separating synthetic organic materials in a
20 mixture, such as various types of filled or unfilled polymers and / or copolymers, including wastes to be recycled for reuse. Such organic materials to be reused originate from the destruction of cars and obsolete durable consumer products at the end of their lives by grinding, and are density separated at a chosen density threshold "ds" to provoke separation, the separation being done in a dense liquid medium
25 formed from stable separative suspensions composed of powder particles dispersed in an aqueous phase.

Other objectives of the invention are to create a method and industrial installation for selectively separating the above mentioned materials by density, such that:

30 ✓ the rheology of separative suspensions remains stable and does not deviate in any way due to fluidisation or thickening of the dense liquid medium,

- √ the apparent density "ds" produced for each separative suspension does not drift due to the destabilisation effect of the suspension in time causing settlement of a variable quantity of the initially dispersed powder particles,
- 5 √ at least almost all powder particles actively and effectively participate in creation of the apparent density of separative suspensions due to their dimensional uniformity, without it being necessary to eliminate particles from the dense liquid medium as they settle, because they are too large and hence they are too heavy,
- 10 √ the selective and precise separation of various synthetic organic materials in a mix to be sorted in which the differential sort sensitivity from one material to another can be as good as $\Delta = |0.001|$ or even the target density value "ds" within ± 0.0005 .

15 Brief description of the invention

According to the various objectives mentioned above, the selective density separation method of synthetic organic waste materials to be recycled for reuse with a density equal to at least 1 and originating from the destruction of cars and durable consumer products at the end of their lives by grinding, household appliances, 20 electronic equipment, is capable of eliminating the disadvantages with the state of the art mentioned above, and at the same time provides substantial improvements not possible with previously described means.

According to the invention, the selective separation method for each constituent of a mix of organic synthetic materials and particularly fragmented 25 waste materials with a density equal to at least 1 and to be reused by recycling, consists of separating them by introducing the said mix into a dense liquid medium that is an aqueous suspension of an appropriate quantity of powder particles dispersed in an aqueous phase, to create a density level "ds" chosen as the separation threshold of the various fragmented synthetic organic materials to be selectively 30 separated by type, characterised in that the said separative suspension is made

selective, stable and having a constant density with a precision of ± 0.0005 about the chosen density threshold "ds" for the selective separation, when it is formed from:

- a) powder particles with a size grading cut-off not more than $30\text{ }\mu\text{m}$, preferably not more than $20\text{ }\mu\text{m}$ and even better not more than $5\text{ }\mu\text{m}$, these solid powder particles thus sized being dispersed and present in the aqueous phase in a sufficient quantity to reach the chosen density threshold "ds",
- b) a water soluble stabiliser to stabilise the rheological and invariance characteristics of the apparent density "ds" with a precision of the said density "ds" of the suspension of solid powder particles equal to ± 0.0005 ,
- c) an aqueous phase.

Detailed description of the invention

The method for selective separation of the mix of synthetic organic waste materials is applicable to all mixed and fragmentated filled or unfilled polymer and / or copolymer materials to be reused, with thermoplastic or thermosetting origin.

With the method according to the invention, the powder particles used in the formation of the aqueous suspension for precise separation of different types of waste synthetic organic materials to be reused in the form of a mix of fragmentated materials, are selected such that:

- ✓ the rheology remains stable in time, in other words there is no significant variation from its initial state towards a more fluid or a denser state,
- ✓ the apparent density "ds" chosen as the precise separation and extraction threshold of a type of waste synthetic organic material from the mix of waste materials containing it, reaches and stays at this apparent density value "ds" with a targeted precision within the interval " $\text{ds} \pm 0.0005$ ", thus resulting in a density sort sensitivity between different materials.

The powder particles used according to the invention may be of natural or synthetic origin.

When the powder particles are of natural origin, they may be chosen from among the group of mineral powder materials formed by clays, that can form a stable

plastic suspension in contact with water, possibly in the groups composed of the kaolinites group for example such as kaolinite, dickite, halloysite, disordered kaolinites, serpentines; the micas group for example such as muscovite, biotite, paragonite, pyrophyllite and talc, illites and glauconite; the montmorillonites group
5 for example such as beidellite, stevensite, saponite, hectorite; the chlorites group, the vermiculites group; the interstratified clays group for which the unit structure is a combination of the previous groups; the fibrous clays group, for example such as attapulgite (palygorskite), sepiolite; or the group consisting of calcium carbonate (calcite), magnesium carbonate, dolomite (double calcium and magnesium
10 carbonate), dehydrated calcium sulphate (gypsum), barium sulphate, talc, alumina, silica, titanium dioxide, zirconia, taken alone or mixed.

Powder particles with a synthetic origin may be selected from among the group consisting of glass powders, precipitated calcium carbonate, metallic powders, taken alone or mixed.

15 The said powder particles used according to the invention must have a size grading cut-off not more than 30 μm , preferably not more than 20 μm and even better not more than 5 μm , so as to create stable suspension conditions by their dispersion in the aqueous phase.

Furthermore, the median diametric dimension of these powder particles could
20 be limited to 5 μm and preferably between 1 μm and 0.005 μm .

Several size grading cut-offs of a single powder component such as calcium carbonate, or several powder compounds such as calcium carbonate and kaolin, can be mixed to refine the separation threshold more precisely at the chosen density "ds".

Similarly, powder particles selected such that the diameter of the majority of
25 particles are within limits recommended in the framework of the invention obtained using a selective sort, can be used to refine the separation threshold more precisely at the chosen density "ds".

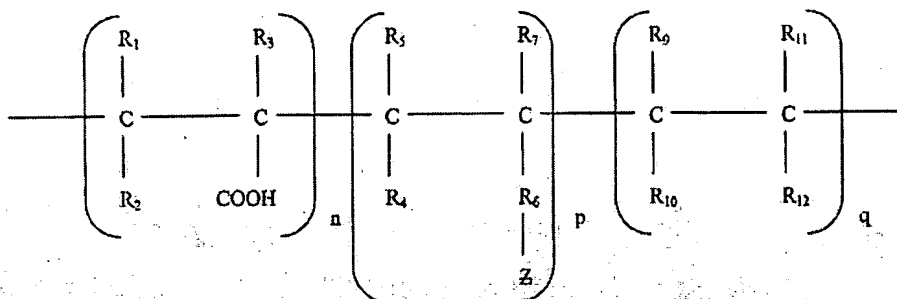
When the dimensional characteristics of the powder particles are greater than the limiting values mentioned above, it becomes clear that the dense separative
30 suspensions obtained by their dispersion in the aqueous phase lead to sedimentation phenomena, unstable characteristics and deviation from the targeted threshold "ds", to achieve the required precise separation of the waste synthetic organic materials.

The quantity by weight of powder particles dispersed in the aqueous phase is dependent on the density threshold "ds" chosen for precise separation of one type of waste polymer materials with a density usually greater than 1, from a mix of waste materials containing it.

5 For example, the quantity of powder particles (ground CaCO_3) necessary to separate unfilled polystyrene (PS) with a density of 1.05 from an unfilled acrylonitrile-butadiene-styrene (ABS) copolymer with a density of 1.07, is 99 g per litre of the aqueous phase to create a precise separation density medium for these two materials with a density "ds" equal to exactly 1.06.

10 With the method according to the invention, the water soluble agent for stabilisation of rheological characteristics and to maintain the apparent density "ds" with a precision of ± 0.0005 about the said density "ds" of the suspension of solid powder particles, is chosen from the group composed of known water soluble stabilisation agents, for example such as phosphates and polyphosphates,
 15 alkylphosphate esters, alkylphosphonate, alkylsulfate, alkylsulfonate esters that cause deflocculation of colloidal clays and enable the use of a high density and low viscosity suspension, lignin, lignosulfonates in the form of calcium, sodium, iron, chromium, iron and chromium salts, copolymers of maleic anhydride and sulfonic styrene acid, substituted, neutralised, esterified or non-esterified copolymers of
 20 methylacrylamide and (methyl) acrylic acid copolymers, sulfonic methylacrylamido-alkyl acid and (methyl) acrylamide acid copolymers, water soluble polymers of acrylic acid used in acid form or possibly wholly or partly neutralised by alkaline and / or alkali earth agents, by amines and / or salified by single-valent and / or polyvalent ions, and / or esterified, or from among water soluble acrylic copolymers
 25 with a phosphated, phosphonated, sulphated or sulfonated pattern.

Preferably, the said water soluble agent may be chosen from among water soluble acrylic copolymers, of which only some are known, satisfying the general formula:



in which:

- 5 ✓ Z is a phosphate, phosphonate, sulphate, sulfonate type pattern with at least one free acid function, any other acid function possibly being occupied by a cation, an ammonium group, an amine, an alkyl in C_1 to C_3 , an aryl in C_3 to C_6 substituted or not, an alkylaryl, an ester in C_1 to C_{12} and preferably in C_1 to C_3 , or a substituted amide.
- 10 ✓ n is equal to a value of between 0 and 95,
- ✓ p is equal to a value of between 95 and 5,
- ✓ q is equal to a value of between 0 and 95,
- ✓ the total value of $n + p + q$ being equal to 100, knowing that n and q may be zero separately,
- 15 ✓ R_1 and R_2 can both be hydrogen simultaneously, or one may be hydrogen while the other may be a carboxylic function that may or may not be esterified by an alcohol in C_1 to C_{12} and preferably in C_1 to C_4 ,
- ✓ R_3 may be hydrogen or an alkyl radical in C_1 to C_{12} and preferably in C_1 to C_4 ,
- 20 ✓ R_4 and R_5 may both simultaneously or separately be hydrogen or an alkyl radical in C_1 to C_{12} and preferably in C_1 to C_4 , a substituted or non-substituted aryl, a carboxylic function that may or may not be esterified by an alcohol in C_1 to C_{12} and preferably in C_1 to C_4 ,
- 25 ✓ R_6 is a radical that sets up the link between the pattern Z and the polymeric chain, this radical R_6 possibly being an alkylene with formula $(CH_2)_r$ in which r may be equal to values in the interval 1 to 12, an oxide

or polyoxide of alkylene with formula $(R_8O)_s$ in which R_8 is an alkylene in C_1 to C_4 and s may be any value from 1 to 30, or a combination of the two formulas $(CH_2)_r$ and $(R_8O)_s$,

- 5 √ R_7 can be hydrogen or an alkyl radical in C_1 to C_{12} and preferably in C_1 to C_4 ,
- √ R_9 and R_{10} may be both simultaneously hydrogen, or one may be hydrogen and the other may be a carboxylic group, an ester in C_1 to C_{12} and preferably in C_1 to C_3 , an alkyl in C_1 to C_{12} and preferably in C_1 to C_3 , an aryl in C_5 or C_6 or an alkylaryl,
- 10 √ R_{11} may be hydrogen, a carboxylic group, an alkyl in C_1 to C_3 or a halogen,
- √ R_{12} may be an ester in C_1 to C_{12} and preferably in C_1 to C_5 , a substituted or non-substituted amide, an alkyl in C_1 to C_{12} and preferably in C_1 to C_3 , an aryl in C_5 or C_6 , an alkylaryl, a halogen, a carboxylic group or an alkyl
- 15 or aryl phosphated, phosphonated, sulphated, sulfonated group.

20 The quantity by weight of the water soluble stabilisation agent is expressed as the dry weight of the said agent as a percentage of the dry weight of powder particles put in suspension. This weight quantity of the said agent is between 0.02% and 5%, and preferably between 0.1% and 2% dry weight of the dry weight of the powder particles.

 The water soluble stabilisation agent is a copolymer with a molecular mass generally between 5000 and 100 000.

25 The water soluble stabilisation agent is in the form of an aqueous copolymer solution that may or may not be partially or wholly neutralised using a neutralisation agent chosen from the group composed of sodium, potassium ammonium, calcium, magnesium hydroxides, and primary, secondary or tertiary, aliphatic and / or cyclic amines such as mono, di, tri ethanolamines, mono and diethylamines, cyclohexylamine, methylcyclohexylamine, etc.

30 With the method according to the invention, the aqueous phase is chosen to be water with a conductivity preferably not more than 50 ms, and even better water with a conductivity of between 0.2 ms and 40 ms, it being understood that the unit

used for the measurement of conductivity is the SIEMENS and that the water measurements used are made in 10^{-3} Siemens, in other words millisiemens, ms.

The aqueous medium used may be chosen from the group consisting of different types of water such as spring water, drinking water, treated or untreated industrial water, possibly but not necessarily circulating in a closed circuit, sea water, knowing that the stability of the suspension at the chosen threshold density "ds" to make a precise separation is achieved when the two criteria, namely (a) the size of the particles, and (b) the presence of a water soluble stabilising agent, are combined.

According to the invention, stable suspensions consisting of an appropriate quantity of dispersed powder particles in an aqueous phase to create a precise density level "ds" chosen as the separation threshold for various synthetic fragmented organic waste materials to be selectively separated based on the precision of the density of the separation medium, are prepared by stirring during the controlled addition of sufficient quantities of powder particles to obtain the required density threshold, in the presence of the water soluble stabilisation agent.

Stable suspensions of powder particles according to the invention,

- enable a precise and selective separation of different synthetic organic materials making up a mix to be sorted,
- for which the sort sensitivity from one material to another may reach a differential $\Delta = |0.001|$
- enable efficient separation of polymer materials, and particularly waste materials to be separated with densities dispersed within the range varying from 1.000 to 1.600.

However, other separation means based on different characteristics or other physicochemical behaviours of the materials have to be used to achieve the said selective separation of different polymer materials and particularly waste materials with exactly the same density but with a different chemical nature.

The method according to the invention is used in an industrial installation comprising at least one hydraulic separator.

A hydraulic separator defines static separators, in other words separators for which the aqueous phase is stagnant or dynamic separators for which the aqueous phase is an active and possibly laminar stream.

If the industrial installation comprises a single hydraulic separator, the chosen density " d_s " can be varied:

- to increase it, by the controlled addition of defined powder particles and the water soluble stabilisation agent, into the suspension present in the hydraulic separator until the new chosen threshold density " d_s " is reached
- to reduce it, by the addition of water until the new chosen threshold density " d_s " is reached.

The density of the separative stable suspension is varied, to increase it or to decrease it, while maintaining mechanical stirring of the dense aqueous medium being corrected and / or while recirculating the dense medium by drawing off from the bottom of the hydraulic separator and reinjection at the top of the said separator.

If the industrial installation comprises several hydraulic separators, the various separators are placed one after the other, using a cascade system operating with stable suspensions each having a precise density threshold " d_s ", in an increasing or decreasing order of the densities.

In controlling the method according to the invention, the threshold density " d_s " of the precise aqueous separative suspension is continuously controlled by appropriate measurement means and is corrected as soon as a drift is detected.

For example, to achieve this, the density of the dense medium contained in each hydraulic separator is controlled using two solenoid valves each opening onto two circuits connected to two reservoirs. One of the reservoirs contains a concentrated "mother " suspension with about 60% of powder particles stabilised with a water soluble stabilisation agent according to the invention, so that a determined quantity of the mother suspension can be added to make an upward correction to any downward drift in the density of the dense precise separation medium.

The other reservoir contains water, and a determined quantity can be added to make a downward correction to any upward drift in the density of the dense precise separation medium.

The density of the dense medium in each hydraulic separator is measured continuously by appropriate measurement instruments that trigger opening of one of the solenoid valves and then close it when the threshold density " d_s " is reached.

The process control and the recovery of separated streams are such that there is no need for any stirring. However, each suspension may be recirculated in each hydraulic separator by drawing off the said suspension at the bottom of the said separator and reinjecting it into the upper part.

5 The separation capacities of the hydraulic separators are of the order of 1 to 10 tonnes per hour and they operate continuously. However, they can operate by campaign and the values of the cut-off densities can then be changed, so that there is not an absolute need for a cascade of more than 3 or 4 hydraulic separators. In this case, the dense medium is custom made for each separator as a function of the
10 separation campaign to be carried out.

Example 1: (conforming with Figure 1)

After most of the various metals to be recovered have been separated on an industrial grinding site for household appliances at the end of their lives, a stream of
15 –22.4 tonnes of reusable materials output from this separation and formed from a mix of waste synthetic polymers to be reused and contaminating materials to be eliminated, is subjected to a preconcentration phase so as to select polymer waste materials to be reused within a density range varying from 1.000 inclusive to 1.200 exclusive to be treated according to the invention from among this mix of waste
20 polymer materials to be reused.

The composition of the material stream used in the preconcentration phase is given in table I below.

Table I

Materials	Ground composition at 25 mm mesh	% content by weight
Polymers	PE, PP, PS, ABS, talc-filled PP, PVC, etc in fragmentated form	65% by weight
Rubber and / or elastomers	All types of seals and / or electrical cable insulating jackets	29% by weight
Metals	Fragments of ferrous metals and	6% by weight

	particularly non-ferrous metals - copper, aluminium, etc.	
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The preconcentration is done on the above-mentioned stream, and consists of treating the mix of fragmentated materials output from grinding, to eliminate at least some of the materials contaminating the reusable materials. The said mix to be
5 treated comprises:

- √ A fraction of reusable synthetic non-expanded polymer materials, with multiple natures and / or compositions and / or shape factors, varying from a rigid state to a flexible state,
- √ Fractions of contaminating materials formed from metallic materials and /
10 or organic materials other than non-expanded polymer materials and / or synthetic polymer materials in an expanded state,

and comprises the following treatment steps:

- a) A first mechanical separation step at (A) by screening and / or shape factor to extract the fraction of contaminating materials, at least from part
15 of the mix of fragmentated materials. The screen mesh was 0 - 4 mm and 0.04 tonnes of contaminating materials were removed representing 0.18% by weight of the input stream.
- b) An aeraulic gas separation step comprising one input of the mix of materials from step a) and three outputs to extract fractions of the
20 separated materials for which the first fraction (b_1) consists of a fraction of ultra-lightweight and / or expanded synthetic polymer materials, the second fraction (b_2) consists of a fraction of heavy materials present in the mix, and the third fraction (b_3) consists of a fraction of synthetic polymer materials to be reused varying from a rigid state to a flexible state. To
25 achieve this, the stream of materials from step a), from which at least part of the fraction of contaminating materials has been removed, was subjected to an aeraulic sort separation in two coupled separators (B) and (C).

In the first aeraulic separator (B), the fraction (b_1) representing 0.52 tonnes of so-called lightweight materials was treated by suction and the fractions b_2 and b_3 extracted through the bottom of the aeraulic separator (B) and representing 21.84 tonnes of so-called heavy materials were collected to be treated in the aeraulic separator (C). The fraction (b_1) represents 2.32% by weight of the lightweight materials eliminated from the input stream.

The mix of fraction (b_2) + (b_3) represents 97.5% by weight of heavy materials.

The mix of the fraction (b_2) and (b_3) representing 20.84 tonnes was added into the second aeraulic sort separator (C). The fraction (b_2) composed of contaminating materials such as metals, etc. representing a mass of 2.82 tonnes, is extracted through the bottom of the aeraulic separator (C).

The fraction (b_3), also extracted from the separator (C) and composed of reusable polymer materials, represents a mass of 19.02 tonnes, namely 84.91% by weight of the input stream to be preconcentrated.

c) A step to grind the fraction (b_3) of polymer materials to be reused output from step b), to the liberation mesh inclusive of contaminating materials bonding to or assembled with fragments of the fraction of polymer materials to be reused. This grinding step is performed in zone (E). Grinding is done on a 25 mm mesh.

d) A second aeraulic gas stream separation step in zone (H) of the fraction of synthetic polymer materials to be reused output from grinding step c) to eliminate at least part of the fraction of contaminating materials released during grinding and to extract the fraction of reusable materials forming the required mix, pre-concentrated in reusable materials still containing contaminants.

This aeraulic separation zone that includes firstly a gas stream separation but also a screening means, contains a modular separation device, for example such as that marketed by the WESTRUP Company.

In this aeraulic separation and screening zone:

- 5 √ A fraction (d_3) representing 18.36 tonnes of reusable synthetic polymer materials, essentially thermoplastics and some thermosetting plastics, was extracted in the form of flakes, chips and other ground materials representing 82% by weight of the total stream entering into the preconcentration,
- √ A fraction (d_2) representing 0.14 tonnes of heavy contaminating materials formed from metals and pieces of electrical wires was eliminated by screening, representing 0.63% by weight of the total stream entering into the preconcentration,
- 10 √ A fraction (d_1) representing 0.52 tonnes of materials that can also be reused was separated by suction, comprising residual polymer foams, thin rubbers, thermoplastic and thermosetting polymer materials in the form of powder, flakes, chips, representing 2.32% by weight of the total stream entering into the preconcentration.

15 The fraction d_3 , a mix of reusable waste synthetic polymers output from step d) but with highly variable densities within a range from 0.900 to 1.400 is exposed to a density separation treatment in an aqueous medium, in zone (J), with a density threshold ≥ 1.2 to make a first density selection.

20 This density separation is done based on a density threshold chosen to be equal to 1.2 in a dense medium formed from an aqueous suspension of powder CaCO_3 dispersed in the aqueous phase and stabilised at the value $ds = 1.2$ using a water soluble stabilisation agent that is a water soluble acrylic copolymer with at least one phosphate function.

 The dense separation medium is composed of:

- 25 √ An aqueous phase with a conductivity of 6.9 ms and a pH of 7.26
- √ Powder calcium carbonate, for which the median diametric dimension is $1\text{ }\mu\text{m}$ and for which the size grading cut-off is $5\text{ }\mu\text{m}$ (OMYALITE 90® marketed by the OMYA Company), at 362 g/litre
- √ the DV 167 water soluble stabilisation agent marketed by the COATEX
- 30 Company, with a dry weight content equal to 0.25% of the dry weight of CaCO_3 .

This separation at the density threshold $ds = 1.2$ leads to two fractions:

- √ a first fraction e_1 with density less than 1.2 representing 17.15 tonnes of reusable materials (76.56% by weight of the input stream), containing in particular polyethylene (PE), polypropylene (PP), impact and / or fire retardant or non-fire retardant crystal polystyrene (PS), fire retardant or non-fire retardant acrylonitrile-butadiene-styrene (ABS) copolymer, polypropylene with 5% to 40% talc filler by weight, and other polymer materials, and
- √ another fraction e_2 with density greater than or equal to 1.2, representing 1.2 tonnes of reusable materials (5.40% by weight of the input stream) in the form of a mix containing polyvinyl chloride, unsaturated filled polyester, filled or other polyurethanes.

The fraction e_1 , a mix of waste polymers to be reused output from step (J), is subjected to a density separation treatment in an aqueous medium in zone (L), at a density threshold $ds = 1.000$ to extract a supernatant stream (f_1) from it consisting of a mix of (PE) and (PP), and a sink stream (f_2) consisting of the other waste polymers to be reused.

The supernatant stream (f_1) that accounts for 23.40% by weight of the fraction (e_1) is subjected to a density separation treatment in a water and alcohol medium (water and isopropanol) at the precise density threshold $ds = 0.930$ in order to recover:

- all the polypropylene present that floats, representing 14.74% by weight of fraction e_1 (2.528 T)
- all polyethylene present that sinks, representing 8.66% by weight of fraction e_1 (1.485 T).

These two finely separated polymer waste materials can be directly reused in the form of pellets obtained by extruding them.

The sink stream (f_2) that accounts for 76.60% by weight of fraction (e_1) formed from an mix unfilled of crystal polystyrene and / or unfilled fire retardant or non-fire retardant impact polystyrene, unfilled acrylonitrile-butadiene-styrene copolymer that is fire retardant for some fractions, and polypropylene filled with 5%

to 40% talc, forms the fraction of polymer waste materials with densities within the interval 1.000 to 1.199 inclusive that are to be separated according to the invention.

The fraction f_2 , a mix of reusable waste synthetic polymers output from the separator (L), is subjected to a density separation treatment in an aqueous medium in
5 zone (N), at a density threshold " $ds = 1.100$ ".

This density separation is done at the chosen density threshold 1.100 in a dense medium formed from an aqueous suspension of powder CaCO_3 dispersed in the aqueous phase and stabilised at the value $ds = 1.100$ using a water soluble stabilisation agent consisting of a water soluble acrylic copolymer with at least one
10 phosphate function.

The dense separation medium is composed of:

- ✓ an aqueous phase with a conductivity of 6.9 ms and a pH of 7.26
- ✓ powder calcium carbonate with a median diametric dimension of $1\ \mu\text{m}$ and for which the size grading cut-off is $10\ \mu\text{m}$ (OMYALITE 50®
15 marketed by the OMYA Company), at 169.5 g/litre.
- ✓ the DV 167 water soluble stabilisation agent marketed by the COATEX Company, with a dry weight content equal to 0.25% of the dry weight of CaCO_3 .

This separation at the density threshold $ds = 1.100$ leads to the following two
20 fractions:

- ✓ A first fraction g_1 with a density less than 1.100 representing 11.317 tonnes of reusable materials (51.82% by weight of the input stream), in particularly containing polystyrene (PS); acrylonitrile-butadiene-styrene (ABS) copolymer, talc-filled polypropylene and other polymer materials,
25 and
- ✓ another fraction g_2 with a density greater than or equal to 1.100, representing 1.820 tonnes of reusable materials (8.13% by weight of the input stream), in the form of a mix containing talc-filled polypropylene, filled and / or fire retardant polystyrene, filled or fire retardant
30 acrylonitrile-butadiene-styrene (ABS) copolymers, or other copolymer materials.

The stream g_1 is actually formed from:

- a mix of crystal or impact polystyrenes, treated or not treated to make them fire retardant, and / or with additives composed of various known agents. This is why the range of densities of these various polystyrenes varies between 1.000 and 1.080.
- a mix of acrylonitrile-butadiene-styrene copolymers for which the actual density depends on the relative quantities of the three monomers used, by any additives and by fire retardant treatments explaining the range of densities of these various (ABS) copolymers, between 1.000 and 1.080.
- a mix of talc-filled polypropylene for which the content of talc as a % by weight may vary from 5% to 20%.

The density range of talc-filled polypropylene is also between 1.000 and 1.080.

This stream g_1 is then subjected to separation by increasing density class using a dense separation medium composed of:

- an aqueous phase with a conductivity of 6.9 ms and a pH of 7.26,
- powder calcium carbonate with a median diametric dimension of 1 μm and for which the size grading cut-off is 5 μm (OMYALATE 90® marketed by the OMYA Company), for which the quantities by weight for each density are expressed in table II below,
- ✓ the water soluble stabilisation agent that is a phosphated water soluble acrylic copolymer marketed by the COATEX company, with a dry weight content equal to 0.25% of the dry weight of CaCO_3 .

The supernatant phase for each known density class represented in table II is recovered and is analysed, and the sink phase is collected and is then input to a density higher than the previous density, so that for each class there is an analysed supernatant phase and a sink phase that in turn is input to a higher density.

Table II:

Density ds fixed as the separation threshold	powder CaCO ₃ in g/l to create ds	Limits of each density class	% by weight in each class		
			of PS	of ABS	of talc- filled PP
1.020	32.30	[1.000 to 1.020[1.20%	0.60%	6.40%
1.042	68.70	[1.020 to 1.042[22.30%	0.00%	16.40%
1.050	82.20	[1.042 to 1.050[35.60%	1.60%	17.20%
1.053	87.30	[1.050 to 1.053[10.00%	3.20%	8.00%
1.055	90.70	[1.053 to 1.055[8.20%	5.60%	3.20%
1.058	95.80	[1.055 to 1.058[4.00%	6.40%	5.20%
1.060	99.20	[1.058 to 1.060[9.10%	14.40%	7.60%
1.065	107.80	[1.060 to 1.065[5.60%	17.20%	10.40%
1.070	116.50	[1.065 to 1.070[2.80%	25.80%	9.20%
1.080	133.90	[1.070 to 1.080[1.20%	24.20%	16.00%
				%	
1.090	151.60	[1.080 to 1.090[0.00%	1.00%	0.40%
1.100	169.50	[1.090 to 1.100[0.00%	0.00%	0.00%
TOTAL			100.00 %	100.00%	100.00%

Quantities of CaCO₃ used in each density class are determined by the density measurement and can vary depending on the purity of the CaCO₃ used.

As shown in table II,

- 5 - most PS is present within the density interval [1.020 - 1.055[forming a first group for crystal PS, but a second density group appears in the [1.055 - 1.070[interval corresponding to impact PS, remembering that some of the PS present is probably fire retardant. These various density classes are statistically justified by the presence of several PS families in this waste polymer to be reused.
- 10

- ABS is also distributed in several density classes, but most ABS present is within the density interval [1.058 - 1.080[. There is also a wide distribution of densities for ABS, due to the presence of several types of ABS for which the composition can vary by the relative quantities of their monomers and also by the presence of fire retarders.
- talc-filled PP is also distributed in several classes due to large density variations caused by the presence of the talc filler that can vary from 5% by weight to 20% by weight.

The mix of polymer waste materials to be reused extracted from each density class in table II is subjected to a new separation by increasing or decreasing density using a dense separation medium, so as to effectively separate the PS, ABS and talc-filled PP present in the same density class, this dense separation medium consisting of:

- An aqueous phase with a conductivity of 6.9 ms and a pH of 7.26,
- Powder calcium carbonate with a median diametric dimension of 1 μm and for which the size grading cut-off is 5 μm (OMYALITE 90® marketed by the OMYA company) and for which quantities by weight are expressed in table III below
- ✓ the DV 167 water soluble phosphated copolymer marketed by the COATEX Company, with a dry weight content equal to 0.25% of the dry weight of CaCO_3 .

For example, only two density separation classes output from table II are selected and treated according to the invention, to illustrate the capacity of the selective separation process for creating stable separative suspensions with invariable density, when the density level "ds" chosen as the separation threshold for the various waste polymer materials to be separated is achieved, the precision of the absolute value of the density can be as good as $|0.001|$, in other words it is possible to achieve a precision about the chosen value "ds" equal to $"ds" \pm 0.0005$.

However, it should be remembered that waste polymers with different chemical natures but exactly the same density cannot be separated by the method

according to the invention and other separation methods based on other criteria are necessary.

The two density classes derived from table II and treated using the method according to the invention are as follows:

- 5 [1.042 to 1.050[
and [1.065 to 1.070[

To achieve this, for each known density class represented in table III, the supernatant phase is recovered and analysed, the sink phase is collected and is then input to a density higher than the previous density, for each class creating an
10 analysed supernatant phase and a sink phase which in turn will be input to a higher density.

This very selective separation gave the results entered class by class in Table III below:

Table III

Density ds defined as the separation threshold	Powder CaCO ₃ in g/l to create ds	Limits of each density class	% by weight in each class		
			PS	ABS	talc- filled PP
1.043	70.40	[1.042-1.043[0.000	0.000	0.609
1.044	72.80	[1.043-1.044[0.000	0.000	0.610
1.045	75.50	[1.044-1.045[0.000	0.000	0.756
1.046	76.20	[1.045-1.046[0.000	0.000	1.025
1.047	77.20	[1.046-1.047[0.000	0.000	0.305
1.048	78.80	[1.047-1.048[0.000	0.000	0.920
1.049	80.50	[1.048-1.049[7.100	0.000	3.050
1.050	82.20	[1.049-1.050[15.125	0.000	9.125
1.066	109.60	[1.065-1.066[1.050	0.115	6.125
1.067	111.30	[1.066-1.067[0.920	0.320	1.952
1.068	113.00	[1.067-1.068[1.250	0.825	1.060
1.069	114.70	[1.068-1.069[1.063	5.690	0.743
1.070	116.50	[1.069-1.070[1.317	10.250	0.520

As shown in table III, the method according to the invention gives excellent control over selective density separation of the polymer materials present in the mix, the sensitivity of the separation density being equal to ± 0.0005 about the chosen density threshold "ds".

However, the initial industrial mix dealt with in this example contains polymer materials with the same density but a different composition, such that other separation means have to be used to separate each type of polymer with identical density present in each fraction.

Example 2: (conforming with Figure 2)

After most of the various metals to be recovered have been separated on an industrial grinding site for household appliances at the end of their lives, a stream of 22.92 tonnes of reusable materials output from this separation and formed from a mix of waste synthetic polymers to be reused and contaminating materials to be eliminated, is subjected to a preconcentration phase as described in example 1 so as to select polymer waste materials to be reused within a density range varying from 1.000 inclusive to 1.600 exclusive to be treated according to the invention from among this mix of polymer waste materials to be reused in order to recover polyvinyl chloride (PVC).

The composition of the material stream used in the preconcentration phase is given in table IV below.

Table IV:

Materials	Ground composition at 25 mm mesh	% content by weight
Polymers	PE, PP, PS, ABS, talc-filled PP, PVC, etc in fragmentated form	19% by weight
Rubber and / or elastomers	All types of seals and / or electrical cable insulating jackets	77% by weight
Metals	Fragments of ferrous metals and particularly non-ferrous metals - copper, aluminium, etc.	4% by weight

The preconcentration is done on the above-mentioned stream, and consists of treating the mix of fragmentated materials originating from grinding, to eliminate at least some of the materials contaminating the reusable materials. The said mix to be treated comprises:

- ✓ A fraction of reusable synthetic non-expanded polymer materials, with multiple natures and / or compositions and / or shape factors, varying from a rigid state to a flexible state,
- ✓ Fractions of contaminating materials formed from metallic materials and / or organic materials other than non-expanded polymer materials and / or synthetic polymer materials in an expanded state,

and comprises the treatment steps as described in example 1:

- a) A first mechanical separation step at (A) by screening and / or shape factor to extract the fraction of contaminating materials, at least from part of the mix of fragmentated materials. The screen mesh was 0 - 4 mm and 0.2 tonnes of contaminating materials were removed representing 0.87% by weight of the input stream.
- b) An aeraulic gas stream separation step to separate the mix of materials output from step a), in two aeraulic separators (B) and (C) coupled together. In the first aeraulic separator (B), fraction (b₁) representing 0.46

tonnes of so-called lightweight materials were treated by suction and the fractions b_2 and b_3 extracted through the bottom of the aeraulic separator (B) and representing 22.26 tonnes of so-called heavy materials were collected to be treated in the aeraulic separator (C). Fraction (b_1) represents 2.01% by weight of the eliminated lightweight materials.

The mix of fractions (b_2) + (b_3) represents 97.12% by weight of heavy materials.

The mix of fractions (b_2) and (b_3) representing 22.26 tonnes was added into the second aeraulic sort separator (C). The fraction (b_2) composed of contaminating materials such as metals, etc. representing a mass of 12.84 tonnes, is extracted through the bottom of the aeraulic separator (C), namely 56.02% of the input stream.

The fraction (b_3), also extracted from the separator (C) and composed of reusable polymer materials, represents a mass of 9.42 tonnes, namely 41.10% by weight of the input stream to be preconcentrated.

- c) a step in zone (E) on the 25 mm mesh, to grind the fraction (b_3) of polymer materials to be reused output from step b), to the liberation mesh inclusive of contaminating materials, sticking to or assembled with fragments of the fraction of polymer materials to be reused.
- d) a second aeraulic gas stream step in the zone (H) to separate the fraction of synthetic polymer materials output from the grinding step c) to be reused. This aeraulic separation step comprises firstly a gas stream separation, and also a screening means (for example a modular separation device made by the WESTRUP Company).

In this aeraulic separation and screening zone (H):

- ✓ A fraction (d_1) representing 4.82 tonnes of materials that can also be reused was separated by suction, and comprises residual polymer foams, thin rubbers, thermoplastic and thermosetting polymer materials in the

form of powder, flakes, chips, representing 21.03% by weight of the total mass stream entering preconcentration,

✓ A fraction (d_2) representing 0.10 tonnes of heavy contaminating materials consisting of metals and pieces of electrical and other wires was eliminated by screening, representing 0.44% by weight of the total mass stream entering preconcentration,

✓ A fraction (d_3) representing 4.50 tonnes of reusable synthetic polymer materials, essentially thermoplastics and a small quantity of thermosetting plastics, was extracted in the form of flakes, chips and other ground forms representing 19.63% by weight of the total mass stream entering into preconcentration.

The fraction d_3 , a mix of reusable waste synthetic polymers output from step d) but with highly variable densities within a range from 0.900 to 1.600 is exposed to a density separation treatment in an aqueous medium, in zone (J), with a density threshold ≥ 1.500 to make a first density selection.

This separation is done based on a density threshold chosen to be equal to 1.500 in a dense medium formed from an aqueous suspension of powder CaCO_3 dispersed in the aqueous phase and stabilised at the value $ds = 1.5$ using a water soluble stabilisation agent that is a water soluble acrylic copolymer with at least one phosphate function.

The dense separation medium is composed of:

- ✓ An aqueous phase with a conductivity of 9.8 ms and a pH of 6.90
- ✓ Powder calcium carbonate, for which the median diametric dimension is $2\text{ }\mu\text{m}$ and for which the size grading cut-off is $20\text{ }\mu\text{m}$ (OMYALITE 90® marketed by the OMYA Company), at 1132 g/litre
- ✓ the DV 167 water soluble stabilisation agent marketed by the COATEX Company, with a dry weight content equal to 0.3% of the dry weight of CaCO_3 .

This separation at the density threshold $ds = 1.5$ leads to two fractions:

√ a first fraction e_1 with density less than 1.5 representing 4.05 tonnes of reusable materials (17.67% by weight of the input stream), containing in particular polyethylene (PE), polypropylene (PP), impact and / or fire retardant or non-fire retardant crystal polystyrene (PS), fire retardant or non-fire retardant acrylonitrile-butadiene-styrene (ABS) copolymer, polypropylene with 5% to 40% talc filler by weight, and other polymer materials, and

√ another fraction e_2 with density greater than or equal to 1.5, representing 0.45 tonnes of reusable materials (1.96% by weight of the input stream) in the form of a mix containing filled polyvinyl chloride, filled or other polyurethanes.

The fraction e_1 , a mix of waste polymers to be reused output from step (J), is subjected to a density separation treatment in an aqueous medium in zone (L), at a density threshold $ds = 1.000$ to extract a supernatant stream (f_1) from it consisting of a mix of (PE) and (PP), and a sink stream (f_2) consisting of the other waste polymers to be reused.

The supernatant stream (f_1) that accounts for 43.46% by weight of the fraction (e_1) is subjected to a density separation treatment in a water and alcohol medium (water and isopropanol):

- at the precise density threshold $ds = 0.930$ in order to recover:
- all the polypropylene present that floats, representing 28.25% by weight of fraction e_1 (1.144 T)
- all polyethylene present that sinks, representing 15.21% by weight of fraction e_1 (0.616 T), the two finely separated waste polymer materials can be directly reused in the form of pellets obtained by extruding them.

The sink stream (f_2) that represents 2,290 T and accounts for 56.54% by weight of fraction (e_1) formed from an unfilled mix of crystal polystyrene and / or fire retardant or non-fire retardant impact polystyrene, unfilled acrylonitrile-butadiene-styrene copolymer that is fire retardant for some fractions, and polypropylene filled with 5% to 40% talc, forms the fraction of waste polymer materials with densities within the interval 1.000 to 1.500 inclusive that are to be separated according to the invention.

The fraction f_2 , a mix of reusable waste synthetic polymers output from the separator (E), is subjected to a density separation treatment in an aqueous medium in zone (N), at a density threshold " $ds = 1.100$ ", to separate and collect part of the PS, ABS and talc-filled PP.

5 This density separation is done at the chosen density threshold 1.100 in a dense medium formed from an aqueous suspension of powder CaCO_3 dispersed in the aqueous phase and stabilised at the value $ds = 1.100$ using a water soluble stabilisation agent consisting of a water soluble acrylic copolymer with at least one phosphate function.

10 The dense separation medium is composed of:

- ✓ an aqueous phase with a conductivity of 9.8 ms and a pH of 6.9
- ✓ Powder calcium carbonate for which the median diametric dimension is $2\text{ }\mu\text{m}$ and for which the size grading cut-off is $20\text{ }\mu\text{m}$ (OMYALITE 50® marketed by the OMYA Company), at 169.5 g/litre.
- 15 ✓ the DV 167 water soluble stabilisation agent marketed by the COATEX Company, with a dry weight content equal to 0.3% of the dry weight of CaCO_3 .

This separation at the density threshold $ds = 1.100$ leads to the following two fractions:

- 20 ✓ A first fraction g_1 with a density less than 1.100 representing 1.44 tonnes of reusable materials (6.47% by weight of the input stream), in particularly containing polystyrene (PS); acrylonitrile-butadiene-styrene (ABS) copolymer, talc-filled polypropylene and other polymer materials, and treated in accordance with the treatment described in example 1 for this fraction, and
- 25 ✓ another fraction g_2 with a density greater than or equal to 1.100, representing 0.85 tonnes of reusable materials (3.71% by weight of the input stream), in the form of a mix containing polyvinyl chloride (PVC), talc-filled polypropylene (more than 20% filler by weight), filled and / or fire retardant polystyrene and acrylonitrile-butadiene-styrene (ABS)
- 30 copolymer, filled polyurethane (PU), filled polyethylene (PE) and others,

that is treated so that each polymer and more particularly PVC can be reused.

The stream g_2 is composed essentially of PVC. This stream g_2 is then added into the series of density class separators (Q) created within the interval [1.100 to 1.500[, in which it is separated by increasing density class using a dense separation medium composed of:

- ✓ An aqueous phase with a conductivity of 9.8 ms and a pH of 6.9
- ✓ Powder calcium carbonate, for which the median diametric dimension is 3 μm and for which the size grading cut-off is 20 μm (OMYALITE 50® marketed by the OMYA Company), for which the weights are expressed for each density in table V below
- ✓ the DV 167 water soluble stabilisation agent marketed by the COATEX Company, with a dry weight content equal to 0.3% of the dry weight of CaCO_3 .

The supernatant phase for each known density class represented in table V is recovered and is analysed, and the sink phase is collected and is then input to a density higher than the previous density, so that for each class there is an analysed supernatant phase and a sink phase that in turn is input to a higher density.

Table V:

Density ds defined as the separation threshold	Powder CaCO_3 in g/l to create ds	Limits of each density class	% by weight in each class	PS	ABS	PP talc	PP	PE	Others	PVC
1.000	0.00	< 1.000	30.6%	0	0	0	19.8	10.8	0	0
		[1.000 - 1.100[22.6%	12.6	6.2	3.8	0	0	0	0
1.100	169.5	[1.100 - 1.350[31%	2	6.2	11.6	0	0	9.7	1.5
1.350	700.0	[1.350 - 1.400[2.8%	0	0	0	0	0	2.4	0.4
1.400	834.5	[1.400 - 1.450[3.5%	0	0	0	0	0	3	0.5
1.450	977.0	> 1.450	9.5%	0	0	0	0	0	9	0.5
TOTAL			100.00 %	14.6	12.4	15.4	19.8	10.8	21.4	2.9

As can be seen in table V, the method according to the invention gives
 5 excellent control over selective density separation of the polymer materials present, the sensitivity of the separation density being equal to ± 0.0005 about the chosen density threshold "ds".

- However, the initial industrial mix considered in this example contains
 10 polymer materials with the same density but a different composition, so that other separation means have to be used to separate the fractions of each polymer type present with the same density.

Example 3:

A synthetic medium was prepared with the composition by weight summarised in table VI, in order to confirm the capability of the method according to the invention for selective separation of the constituents of a mix of synthetic organic materials consisting of different types of polymers, some of which have a very similar density, in a dense liquid medium:

Table VI

Polymer	Measured density	<u>Synthetic mixes</u>	
		kg added	% by weight
Ethylene-propylene copolymer	0.900	350	46.06
Polystyrene	1.050	100	13.16
Ethylene-propylene copolymer with 20% talc filler	1.060	150	19.73
Acrylonitrile-butadiene-styrene copolymer	1.070	80	10.53
Polyamide 6	1.13	40	5.26
Polyvinyl chloride	1.38	40	5.26
Total		760	100%

This mix is subjected to a density separation treatment in a dense liquid medium consisting of an aqueous suspension of powder CaCO_3 dispersed in the aqueous phase and stabilised at the chosen density value ds using a water soluble stabilisation agent that is a water soluble acrylic copolymer with at least a phosphate function.

The dense separation medium is composed of:

- An aqueous phase with a conductivity of 6.9 ms and a pH of 7.26

- Powder calcium carbonate with a median diametric dimension of 1 μm and for which the size grading cut-off is 5 μm (OMYALITE 90® marketed by the OMYA company), using the quantities in g/l necessary to create increasing values of the density "ds" of the dense medium, starting from the initial value ds = 1.000 up to the value ds = 1.200 to achieve selective separation.
- the DV 167 water soluble stabilisation agent marketed by the COATEX Company, with a dry weight content equal to 0.25% of the dry weight of CaCO_3 .

The selective separation is then made through increasing density thresholds "ds" to obtain two polymer fractions for each density threshold "ds", one supernatant with a density of less than "ds" and the other sinking with a density greater than "ds". All information about these selective separations is given in table VII below:

Table VII:

Density ds fixed as the separation threshold	Powder CaCO_3 in g/l to create ds	Types and quantities of selectively separated polymers	% polymers recovered with respect to the initial synthetic mix
1.000	0.00	348 kg of copolymer (E/P)	99.4
1.055	90.70	99 kg of PS	99.0
1.065	107.80	148.6 kg of copolymer (E/P) 20% talc	99.1
1.075	125.20	79.0 kg of ABS	98.8
1.200	361.60	39.5 kg of PA 6	98.8
< 1200		39.6 kg of rigid PVC	99.0

As can be seen, selective separation of the various polymers present in the initial synthetic mix by increasing density class of an aqueous suspension of CaCO_3 in the presence of a suspension stabilisation agent, is precise and efficient, because each polymer present in the initial mix is selectively extracted for each chosen density threshold "ds" for this purpose, without entraining any particular polymer into adjacent classes, each selective separation class having operated precisely according to forecasts and containing only the selected polymer.

Compared with the total mass of the initial synthetic mix (760 kg), the loss of polymers during the selective separation using the method according to the invention is 6.3 kg, in other words 0.83% by weight.

Example 4: (conforming with Figure 1)

After most of the various metals to be recovered have been separated on the same industrial grinding site as in example 1 for household appliances at the end of their lives, a stream of 22.4 tonnes of reusable materials formed from a mix of waste synthetic polymers to be reused and contaminating materials, is subjected to a preconcentration phase so as to extract waste polymer materials to be reused within a density range varying from 1.000 to 1.200 to be treated according to the invention from among this mix of waste polymer materials to be reused.

The composition of the material stream used in the preconcentration phase is given in table VIII below.

Table VIII:

Materials	Ground composition at 25 mm mesh	% content by weight
Polymers	PE, PP, PS, ABS, talc-filled PP, PVC, etc in comminuted form	65% by weight
Rubber and / or elastomers	All types of seals and / or electrical cable insulating jackets	29% by weight

Metals	Fragments of ferrous metals and particularly non-ferrous metals - copper, aluminium, etc.	6% by weight
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Preconcentration is done in the same way as in example 1, starting from the above mentioned mix including:

- 5 √ A fraction of reusable synthetic non-expanded polymer materials, with multiple natures and / or compositions and / or shape factors, varying from a rigid state to a flexible state,
- √ Fractions of contaminating materials formed from metallic materials and / or organic materials other than non-expanded polymer materials and / or synthetic polymer materials in an expanded state, comprising treatment
- 10 steps a) to d) according to example 1.

a) In the first mechanical separation step at (A) by screening and / or shape factor, 0.04 tonnes of contaminating materials were extracted representing 0.18% of the input stream.

- 15 b) In step b), the material stream from step a) from which at least part of the fraction of contaminating materials has been removed, was separated by aeraulic sort in two coupled separators (B) and (C).

In the first aeraulic separator (B), the fraction (b_1) representing 0.52 tonnes of so-called lightweight materials was treated by suction, and fractions b_2 and b_3 extracted through the bottom of the aeraulic separator (B) and representing 21.84

20 tonnes of so-called heavy materials, were collected to be treated in the aeraulic separator (C). The fraction (b_1) represents 2.32% by weight of lightweight materials eliminated from the input stream.

The mix of fractions (b_2) + (b_3) represents 97.5% by weight of heavy materials.

25 The mix of fractions (b_2) and (b_3) representing 20.84 tonnes was added into the second aeraulic sort separator (C). The fraction (b_2) composed of contaminating materials such as metals, representing a mass of 2.82 tonnes, is extracted through the bottom of the aeraulic separator (C).

The fraction (b_3), also extracted from the separator (C) and composed of reusable polymer materials, represents a mass of 19.02 tonnes, namely 84.91% by weight of the input stream to be preconcentrated.

5 c) The step to grind the fraction (b_3) of polymer materials to be reused originating from step b), to the contaminating materials liberation mesh inclusive, is done in zone (E), grinding being done on a 25 mm mesh.

d) The second aeraulic gas stream step to separate the fraction of synthetic polymer materials to be reused output from the grinding step c) is done in zone (H), to at least partly eliminate the fraction of contaminating materials released during
10 grinding and to extract the fraction of reusable materials forming the required mix, pre-concentrated into reusable materials still containing contaminants.

This aeraulic separation zone (H) comprises firstly a gas stream separation and also a screening means, and is formed by a modular separation device for example like that marketed by the WESTRUP Company.

15 In this separation zone (H):

- ✓ A fraction (d_3) representing 18.36 tonnes of reusable synthetic polymer materials was extracted, representing 82% by weight of the total mass of the stream input into the preconcentration,
- ✓ A fraction (d_2) representing 0.14 tonnes of heavy contaminating materials
20 formed from metals and pieces of electrical wires was eliminated, representing 0.63% by weight of the total stream entering into the preconcentration,
- ✓ A fraction (d_1) representing 0.52 tonnes of materials that can also be reused was separated by suction, comprising residual polymer foams, thin
25 rubbers, thermoplastic and thermosetting polymer materials, representing 2.32% by weight of the total stream entering into the preconcentration.

The fraction d_3 , a mix of reusable waste synthetic polymers output from step d) but with highly variable densities within a range from 0.900 to 1.400 is exposed to a density separation treatment in an aqueous medium, in zone (J), with a density
30 threshold ≥ 1.2 to make a first density selection.

This separation is done based on a density threshold chosen to be equal to 1.2 in a dense medium formed from an aqueous suspension of powder kaolin dispersed in the aqueous phase and stabilised at the value $ds = 1.2$ using a water soluble stabilisation agent that is a water soluble acrylic copolymer with at least one phosphate function.

The dense separation medium is composed of:

- ✓ An aqueous phase with a conductivity of 6.9 ms and a pH of 7.26
- ✓ Kaolin, for which the median diametric dimension is $1\ \mu\text{m}$ and the size grading cut-off is $30\ \mu\text{m}$, at 373.29 g/litre
- ✓ the DV 167 water soluble stabilisation agent marketed by the COATEX Company, with a dry weight content equal to 0.25% of the dry weight of kaolin.

This separation at the density threshold $ds = 1.2$ leads to two fractions:

- ✓ a first fraction e_1 with density less than 1.2 representing 17.20 tonnes of reusable materials (76.78% by weight of the input stream), containing in particular polyethylene (PE), polypropylene (PP), impact and / or fire retardant or non-fire retardant crystal polystyrene (PS), fire retardant or non-fire retardant acrylonitrile-butadiene-styrene (ABS) copolymer, polypropylene with 5% to 40% talc filler by weight, and other polymer materials, and
- ✓ another fraction e_2 with density greater than or equal to 1.2, representing 1.16 tonnes of reusable materials (5.18% by weight of the input stream) in the form of a mix containing polyvinyl chloride, unsaturated filled polyester, filled or other polyurethanes.

The fraction e_1 , a mix of waste polymers to be reused output from step (J), is subjected to a density separation treatment in an aqueous medium in zone (L), at a density threshold $ds = 1.000$ to extract a supernatant stream (f_1) from it consisting of a mix of (PE) and (PP), and a sink stream (f_2) consisting of the other waste polymers to be reused.

The supernatant stream (f_1) that accounts for 23.50% by weight of the fraction (e_1) is subjected to a density separation treatment in a water and alcohol medium

(water and isopropanol) at the precise density threshold $ds = 0.930$ in order to recover:

- all the polypropylene present that floats, representing 14.76% by weight of fraction e_1 (2.54 T)
- 5 - all polyethylene present that sinks, representing 8.74% by weight of fraction e_1 (1.50 T).

These two finely separated waste polymer materials can be directly reused in the form of pellets obtained by extruding them.

10 The sink stream (f_2) that accounts for 76.50% by weight of fraction (e_1) formed from an unfilled mix of crystal polystyrene and / or fire retardant or non-fire retardant impact polystyrene, unfilled acrylonitrile-butadiene-styrene copolymer that is fire retardant for some fractions, and polypropylene filled with 5% to 40% talc, forms the fraction of waste polymer materials with densities within the interval 1.000 to 1.199 inclusive that are to be separated according to the invention.

15 The fraction f_2 , a mix of reusable waste synthetic polymers output from the separator (L), is subjected to a density separation treatment in an aqueous medium in zone (N), at a density threshold " $ds = 1.100$ ".

20 This separation is done at the chosen density threshold 1.100 in a dense medium formed from an aqueous suspension of powder kaolin dispersed in the aqueous phase and stabilised at the value $ds = 1.100$ using a water soluble stabilisation agent consisting of a water soluble acrylic copolymer with at least one phosphate function.

The dense separation medium is composed of:

- ✓ an aqueous phase with a conductivity of 6.9 ms and a pH of 7.26
- 25 ✓ kaolin carbonate, for which the median diametric dimension is 1 μm and for which the size grading cut-off is 30 μm , at 174.2 g/litre
- ✓ the DV 167 water soluble stabilisation agent marketed by the COATEX Company, with a dry weight content equal to 0.25% of the dry weight of CaCO_3 .

30 This separation at the density threshold $ds = 1.100$ leads to two fractions:

- √ a first fraction g_1 with density less than 1.100 representing 11.45 tonnes of reusable materials (51.12% by weight of the input stream), containing in particular polystyrene (PS), acrylonitrile-butadiene-styrene (ABS) copolymer, polypropylene with talc filler, and other polymer materials, and
- √ another fraction g_2 with density greater than or equal to 1.100, representing 1.75 tonnes of reusable materials (7.81% by weight of the input stream) in the form of a mix containing talc-filled polypropylene, filled and / or fire retardant polystyrene, filled or fire retardant acrylonitrile-butadiene-styrene (ABS) copolymers, or other copolymer materials.

The stream g_1 is actually formed from:

- a mix of crystal or impact polystyrenes, treated or not treated to make them fire resistant and containing additives consisting of various known agents. This is why the range of densities of these various polystyrenes is between 1.000 and 1.080.
- a mix of acrylonitrile-butadiene-styrene copolymers, for which the genuine density is determined by the relative quantities of the three monomers used, any additives and fire retardant treatments, explaining the range of densities of these various (ABS) products that varies between 1.000 and 1.080.
- a mix of talc-filled polypropylene with a talc content as a % by weight varying from 5% to 20%. The density range of talc-filled polypropylene is also between 1.000 and 1.080.

This stream g_1 is then subjected to separation by increasing density class using the dense separation medium comprising:

- an aqueous phase with a conductivity of 6.9 ms and a pH of 7.26,
- powder kaolin with a median diametric dimension of 1 μm and for which the size grading cut-off is 30 μm , for which the quantities by weight for each density are given in table II below

- the water soluble phosphated acrylic copolymer stabilisation agent marketed by the COATEX company, with a dry weight content equal to 0.25% of the dry weight of kaolin.

5 To achieve this, for each known density class represented in table IX, the supernatant phase is recovered and analysed, the sink phase is collected and is then input to a density higher than the previous density, for each class creating an analysed supernatant phase and a sink phase which in turn will be input to a higher density.

Table IX:

Density ds fixed as the separation threshold	kaolin in g/l powder to create ds	Limits of each density class	% by weight in each class		
			PS	ABS	talc-filled PP
1.020	33.08	[1.000 to 1.020[1.25%	0.60%	6.40%
1.042	70.09	[1.020 to 1.042[22.30%	0.00%	16.50%
1.050	83.87	[1.042 to 1.050[35.55%	1.60%	17.15%
1.053	89.08	[1.050 to 1.053[10.08%	3.25%	8.05%
1.055	92.56	[1.053 to 1.055[8.25%	5.65%	3.10%
1.058	97.80	[1.055 to 1.058[3.95%	6.35%	5.25%
1.060	101.3	[1.058 to 1.060[9.05%	14.40%	7.60%
1.065	110.10	[1.060 to 1.065[5.62%	17.10%	10.35%
1.070	118.95	[1.065 to 1.070[2.75%	25.80%	9.30%
1.080	136.94	[1.070 to 1.080[1.20%	24.25%	15.900%
1.090	154.97	[1.080 to 1.090[0.00%	1.00%	0.40%
1.100	173.33	[1.090 to 1.100[0.00%	0.00%	0.00%
TOTAL			100%	100%	100%

The quantities of kaolin used in each density class are determined by the density measurement and can vary depending on the purity of the kaolin used.

As shown in table IX:

- 5 - most PS is present within the density interval [1.020 - 1.055[forming a first group for crystal PS, but a second density group appears in the [1.055 - 1.070[interval corresponding to impact PS, remembering that some of the PS present is probably fire retardant. These various density classes are statistically justified by the presence of several PS families in this waste polymer to be reused.
- 10 - ABS is also distributed in several density classes, but most ABS present is within the density interval [1.058 - 1.080[. There is also a wide distribution of densities for ABS, due to the presence of several types of

ABS for which the composition can vary by the relative quantities of their monomers and also by the presence of fire retarders.

- talc-filled PP is also distributed in several classes due to large density variations caused by the presence of the talc filler that can vary from 5% by weight to 20% by weight.

The mix of waste polymer materials to be reused extracted from each density class in table II is subjected to a new separation by increasing or decreasing density using a dense separation medium, so as to effectively separate the PS, ABS and talc-filled PP present in the same density class, this dense separation medium consisting of:

- An aqueous phase with a conductivity of 6.9 ms and a pH of 7.26,
 - Powder kaolin with a median diametric dimension of 1 μm and for which the size grading cut-off is 30 μm and for which quantities by weight are expressed in table III below
- ✓ the DV 167 water soluble phosphated copolymer marketed by the COATEX Company, with a dry weight content equal to 0.25% of the dry weight of CaCO_3 .

For example, only two density separation classes output from table II are selected and treated according to the invention, to illustrate the capacity of the selective separation process for creating stable separative suspensions with invariable density, when the density level "ds" chosen as the separation threshold for the various waste polymer materials to be separated is achieved, the precision of the absolute value of the density can be as good as $|0.001|$, in other words it is possible to achieve a precision about the chosen value "ds" equal to $"ds" \pm 0.0005$.

However, it should be remembered that waste polymers with different chemical natures but exactly the same density cannot be separated by the method according to the invention and other separation methods based on other criteria are necessary.

The two density classes derived from table II and treated using the method according to the invention are as follows:

[1.042 to 1.050[

and [1.065 to 1.070[

To achieve this, for each known density class represented in table X, the supernatant phase is recovered and analysed, the sink phase is collected and is then input to a density higher than the previous density, for each class creating an analysed supernatant phase and a sink phase which in turn will be input to a higher density.

This very selective separation gave the results entered class by class in Table X below:

10 Table X:

Density ds fixed as the separation threshold	kaolin in g/l powder to create ds	Limits of each density class	% by weight in each class		
			PS	ABS	talc- filled PP
1.043	72.16	[1.042-1.043[0	0	0.608
1.044	73.89	[1.043-1.044[0	0	0.610
1.045	75.62	[1.044-1.045[0	0	0.754
1.046	77.35	[1.045-1.046[0	0	1.027
1.047	79.08	[1.046-1.047[0	0	0.307
1.048	80.81	[1.047-1.048[0	0	0.920
1.049	82.55	[1.048-1.049[7.12	0	3.049
1.050	84.29	[1.049-1.050[15.105	0	9.125
1.066	112.42	[1.065-1.066[1.052	0.113	6.125
1.067	114.20	[1.066-1.067[0.920	0.320	1.950
1.068	115.98	[1.067-1.068[1.248	0.827	1.058
1.069	117.76	[1.068-1.69[1.065	5.686	0.745
1.070	119.55	[1.069-1.070[1.315	10.254	0.522

As shown in table X, the method according to the invention gives excellent control over selective density separation of the polymer materials present in the mix,

the sensitivity of the separation density being equal to ± 0.0005 about the chosen density threshold "ds".

However, the initial industrial mix dealt with in this example contains polymer materials with the same density but a different composition, such that other
5 separation means have to be used to separate each type of polymer with identical density present in each fraction.